FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 25065-27

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): 10/030881

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/RU99/00368	08 OCT 99 (08.10.99)	22 APRIL 99 (22.04.99)

TITLE OF INVENTION: **ZIRCONIUM-BASED ALLOY ELEMENTS USED IN NUCLEAR REACTOR CORES**

APPLICANT(S) FOR DO/EO/US: **NIKULINA, Antonina Vasilievna, et al**

I hereby certify that this paper or fee is being deposited with the U.S. Postal Service "Express Mail" Post Office to Addressee" service under 37 CFR 1.10 on the date indicated below and addressed to the Commissioner of Patents and Trademarks, Washington, DC 20231.

Brigid Mullins

DATE 22 October 2001

EXPRESS MAIL NO. EL035783419US

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). (SEE BELOW)
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) (SEE BELOW)
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

The translation filed herewith is submitted as received by the attorney of record, who has been unable to determine, as yet, whether amendments to the claims were made during the international phase of prosecution.

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/030861	PCT/RU99/00368	25065-27

531 Rec'd PCT/PTO 22 OCT 2001

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**	
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**	
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**	
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**	
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	

ENTER APPROPRIATE BASIC FEE AMOUNT =	**$1,040.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	8 - 20 =	0	x $18.00	**$0.00**	
Independent claims	3 - 3 =	0	x $80.00	**$0.00**	
Multiple Dependent Claims **(check if applicable)**			☐	**$0.00**	

TOTAL OF ABOVE CALCULATIONS =	**$1,040.00**	
☐ Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.	**$0.00**	
SUBTOTAL =	**$1,040.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +	**$0.00**	
TOTAL NATIONAL FEE =	**$1,040.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐	**$0.00**	
TOTAL FEES ENCLOSED =	**$1,040.00**	
	Amount to be: refunded	$
	charged	$

a. ☒ A check in the amount of **$1,040.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **08-0719** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

John B. Hardaway, III
NEXSEN PRUET JACOBS & POLLARD, LLC
P.O. Box 10107
Greenville, SC 29603

SIGNATURE

J. Herbert O'Toole
NAME

31,404
REGISTRATION NUMBER

October 22, 2001
DATE

BEFORE THE UNITED STATES PATENT AND TRADEMARK OFFICE
APPLICATION FILED UNDER THE PATENT COOPERATION TREATY
U.S NATIONAL PHASE OF PROSECUTION
EO/US

APPLICANT:	NIKULINA, Antonina Vasilievna, et al
INTERNATIONAL APPL. NO.:	PCT/RU99/00368
INTERNATIONAL FILING DATE:	08 OCTOBER 1999 (08.10.99)
TITLE:	ZIRCONIUM-BASED ALLOY ELEMENTS USED IN NUCLEAR REACTOR CORES
ATTORNEY DOCKET NO.:	25065-27

Assistant Commissioner for Patents
Box PCT
Washington, DC 20231
ATTN: EO/US

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Brigid Mullins
DATE: 22 October 2001
EXPRESS MAIL NO. EL035783419US

PRELIMINARY AMENDMENT

Dear Sir:

Prior to figuring the filing fee and prior to examination of the U.S national entry application arising from the referenced international application, please enter the amendment on the following pages, removing multiple dependency from the claims.

Claims 1 - 6 are amended. Claims 7 and 8 are new. In addition, a copy of the claims as received by the attorney of record is attached, marked to show the amendments.

Respectfully submitted,

J. Herbert O'Toole
Agent/Attorney for Applicant
31404

Date: 22 October 2001

CLAIMS

1. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, comprising niobium, iron, oxygen, carbon and silicon, featured by a structure comprising an α-solid zirconium solution, which comprises nickel, with the following ratio of the constituents (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

and the structure of the alloy further comprises particles of the β Nb-phase which are sized below 0.1 μm and are uniformly distributed in said α-solid zirconium solution.

2. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, according to claim 1 wherein the structure further comprises particles of intermetallics Zr-Fe-Nb.

3. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, which comprises constituents taken with the following ratio therebetween (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the niobium content of the β Nb-phase particles being within 79 to 95%.

4. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, which comprises said constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.02 - 0.5
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the iron/niobium ration being 0.05:0.2.

5. (Amended) A zirconium-based alloy for components of the active core of nuclear reactors according to claim 3 which comprises said constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.005 - 0.5
oxygen	0.1 - 0.2
carbon	0.001 - 0.02
silicon	0.002 - 0.1
nickel	0.003 - 0.02
zirconium	being the balance,

with the niobium content of the β-particles in the Nb-phase ranging between 75 and 95%, the α-solid solution being further oxygen-hardened.

6. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors according to claim 2, wherein the size of the particles of intermetallics Zr-Fe-Nb is below 0.3 μm.

7. (New) A zirconium-based alloy for the components of the active core of nuclear reactors according to claim 4 wherein the size of the particles of intermetallics Zr-Fe-Nb is below 0.3 μm.

8. (New) A zirconium-based alloy for the components of the active core of nuclear reactors according to claim 5 wherein the size of the particles of intermetallics Zr-Fe-Nb is below 0.3 μm.

CLAIMS

1. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, comprising niobium, iron, oxygen, carbon and silicon, featured by a structure comprising an a-solid zirconium solution, [CHARACTERIZED in that said alloy further] which comprises nickel, with the following ratio of the constituents (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

and the structure of the alloy further comprises particles of the β Nb-phase which are seized below 0.1 μm and are uniformly distributed in said α-solid zirconium solution.

2. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, according to claim 1 [CHARACTERIZED in that its] wherein the structure further comprises particles of intermetallics Zr-Fe-Nb.

3. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, [CHARACTERIZED in that it] which comprises [said] constituents taken with the following ratio therebetween (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the niobium content of the β Nb-phase particles being within 79 to 95%.

4. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors, [CHARACTERIZED in that it] which comprises said constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.02 - 0.5
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the iron/niobium ration being 0.05:0.2.

5. (Amended) A zirconium-based alloy for components of the active core of nuclear reactors, [CHARACTERIZED in that it] according to claim 3 which comprises said constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.005 - 0.5
oxygen	0.1 - 0.2
carbon	0.001 - 0.02
silicon	0.002 - 0.1
nickel	0.003 - 0.02
zirconium	being the balance,

with the niobium content of the β-particles in the Nb-phase ranging between 75 and 95%, the α-solid solution being further oxygen-hardened.

6. (Amended) A zirconium-based alloy for the components of the active core of nuclear reactors [as claimed in any one of] according to [claims 2, 4, and 4,] claim 2, wherein [CHARACTERIZED in that] the size of the particles of intermetallics Zr-Fe-Nb is below 0.3 μm.

PCT

ВСЕМИРНАЯ ОРГАНИЗАЦИЯ ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ
Международное бюро

МЕЖДУНАРОДНАЯ ЗАЯВКА, ОПУБЛИКОВАННАЯ В СООТВЕТСТВИИ С ДОГОВОРОМ О ПАТЕНТНОЙ КООПЕРАЦИИ (PCT)

(51) Международная классификация изобретения [7]: C22C 16/00, G21C 3/07	A1	(11) Номер международной публикации: **WO 00/65116** (43) Дата международной публикации: 2 ноября 2000 (02.11.00)

(21) **Номер международной заявки:** PCT/RU99/00368

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(30) **Данные о приоритете:**
99107802 22 апреля 1999 (22.04.99) RU

(71) **Заявитель** *(для всех указанных государств, кроме (US):* ГОСУДАРСТВЕННЫЙ НАУЧНЫЙ ЦЕНТР РОССИЙСКОЙ ФЕДЕРАЦИИ ВСЕРОССИЙСКИЙ НАУЧНО-ИССЛЕДОВАТЕЛЬСКИЙ ИНСТИТУТ НЕОРГАНИЧЕСКИХ МАТЕРИАЛОВ ИМЕНИ АКАДЕМИКА А.А.БОЧВАРА [RU/RU]; 123060 Москва, а/я 369 (RU) [GOSUDARSTVENNY NAUCHNY TSENTR ROSSIISKOI FEDERATSII NAUCHNO-ISSLEDOVATELSKY INSTITUT NEORGANICHESKIKH MATERIALOV IMENI AKADEMIKA A.A.BOCHVARA, Moscow (RU)].

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(81) **Указанные государства:** CA, GH, IN, JP, KR, UA, US, европейский патент (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Опубликована
С отчётом о международном поиске.

(54) **Title:** ZIRCONIUM-BASED ALLOY FOR ELEMENTS USED IN NUCLEAR REACTOR CORES

(54) **Название изобретения:** СПЛАВ НА ОСНОВЕ ЦИРКОНИЯ ДЛЯ ЭЛЕМЕНТОВ АКТИВНОЙ ЗОНЫ АТОМНЫХ РЕАКТОРОВ

(57) **Abstract:**

The present invention relates to a zirconium-based alloy which is intended for elements used in nuclear reactor cores and comprises the following elements: from 0.5 to 3.0 wt % of niobium; from 0.005 to 0.5 wt % of iron; from 0.03 to 0.2 wt % of oxygen; from 0.001 to 0.04 wt % of carbon; from 0.002 to 0.1 wt % of silicon; from 0.003 to 0.02 wt % of nickel; the balance consisting of zirconium. The alloy structure is characterised in that it has a α-hardness temper and contains β Nb-phase particles having a size not exceeding 0.1 μm, the base having a niobium content of 60 to 95 %. This alloy may also includes particles of Zr-Fe-Nb intermetallic compounds, wherein the ratio between the iron and the niobium ranges from 0.05 to 0.2. This alloy structure may also be characterised by a α-hardness temper reinforced by oxygen and by β Nb-phase particles and may also include particles of Zr-Fe-Nb intermetallic compounds having a size not exceeding 0.3 μm.

ZIRCONIUM-BASED ALLOY ELEMENTS USED IN NUCLEAR REACTOR CORES

Technical Field

The present invention relates to metallurgy, more particularly to zirconium-based alloys used in the active core of nuclear reactors.

Background Art

Zirconium-based alloys find application as construction elements of the active core of nuclear power reactors operating on thermal neutrons, such as fuel claddings, pipes for process channels, and other construction elements.

Quite a number of requirements are imposed upon the alloys mentioned above, that is, as to corrosion resistance in water and high-temperature steam, strength characteristics, resistance to oxidation, hydrogenation, radiation growth, and creep. In addition, the alloy must possess high processability.

Known in the present state of the art is a zirconium-based alloy containing 1-4 wt.% niobium and 0.1-0,2 wt.% oxygen and consisting predominantly of a martensitic transformation of the β-phase and a finely dispersed secondary phase rich in niobium (cf. GB Pat. A No 997761).

Products made from said known alloy feature but an inadequately broad complex of anticorrosion properties, including inadequately high resistance to nodular corrosion in boiling water.

Another zirconium-based alloy is known to comprise (on a weight percent basis): niobium, 0.5 - 1.5; tin, 0.9 - 1.5; iron, 0.3 - 0.6; chromium, 0.005 - 0.2; carbon, 0.005 - 0.04; oxygen, 0.05 - 0.15; silicon, 0.005 - 0.15, the structure of said alloy being a metallic matrix hardened with niobium- and iron-containing intermetallics having the following volumetric content of the sum of intermetallics: $Zr(Fe,Nb)_2$ +

$Zr(Fe,Cr,Nb) + (Zr,Nb)_3Fe$ being at least 60% of a total content of the iron-containing intermetallics and a distance therebetween equal to 0.322 ± 0.09 μm (cf. RU Pat. A No 2032759).

Products made from said known alloy feature high strength characteristics, resistance to radiation growth, creep, and rust-proof quality. However, corrosion in a water medium affecting the products made of said known alloy results in forming a thicker oxide layer than is observed in the proposed alloy.

One more zirconium-based alloy is known to comprise (on the weight percent basis): niobium, 0.8 - 1.3; iron, 0.005 - 0.025; silicon, below 0.012; carbon, below 0.02; oxygen, below 0.16, zirconium being the balance (cf. EP A 0720177 A1).

This technical solution as being the closest to the herein-claimed one as to technical essence, is elected to be the prototype.

Products made of the alloy known from the prototype possess but an inadequately broad complex of anticorrosion and mechanical properties. A reduced niobium and iron content prevents preparing a structure that imparts high corrosion resistance to the alloy, especially resistance to nodular corrosion, as well as high strength and creep- and radiation growth resistance.

Disclosure of the Invention

The principal object of this invention is the provision of a zirconium-based alloy for the components of the active core of nuclear reactors, the products made of said alloy possess stable properties, such as corrosion resistance, hardness, resistance to radiation growth and creep, and substantially high resistance to nodular corrosion, whereby the service life of the products in the active core of a nuclear reactor is substantially extended.

Said object is accomplished due to the fact that a zirconium-based alloy for the components of the active core of nuclear reactors,

comprising niobium, iron, oxygen, carbon, and silicon, according to the invention, further comprises nickel, with the following ratio of the components (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

and the structure of the alloy further comprises β-particles of the Nb-phase which are sized less than 0.1 μm and are uniformly distributed in the α-solid solution, while said phase has a niobium percentage content of from 60 to 95. The structure may also further comprise intermetallic particles Zr-Fe-Nb sized less than 0.3 μm.

The alloy may be constituted by the following constituents taken in the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

with the niobium content of the beta-particles in the Nb-phase ranging between 75 and 95%.

The alloy may be constituted by the following constituents taken in the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.02 - 0.5
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the iron/niobium ratio being 0.05:0.2.

The alloy may be constituted by the following constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.005 - 0.5
oxygen	0.1 - 0.2
carbon	0.001 - 0.02
silicon	0.002 - 0.1
nickel	0.003 - 0.02
zirconium	being the balance,

with the niobium content of the β-particles in the Nb-phase ranging between 75 and 95% and the α-solid solution being further oxygen-hardened.

The alloy proposed herein, in contradistinction to the prototype, allows one to obtain an optimum structure-phase state which provides for high corrosion resistance in water and steam media, as well as high hardness, creep- and radiation growth resistance.

Making products from the herein-proposed alloy by virtue of more exactly selected ratio between the constituents constituting said alloy enables one to create a definite alloy structure in finished products, which structure comprises α-solid solution of zirconium, uniformly distributed finely divided particles of the equilibrium β Nb-phase, solid solution of zirconium in niobium having a body-centered cubic lattice

with the parameter 'a' equal to 3.3 – 3.35 Å and the niobium content in excess of 75% which corresponds to an equilibrium composition of the β Nb-phase. The structure of the material may also incorporate finely divided particles of intermetallics Zr-Fe-Nb.

The herein-proposed chemical analysis of the alloy and the presence of the β Nb-phase therein the particles of which are sized below 0.1 μm, the niobium content of said phase ranging within 75 and 95%, provides for establishing an equilibrium and superfine structure, thus adding to the stability of in-service characteristics of finished products, especially such characteristics as corrosion resistance and plasticity.

The 75 to 95% niobium content of the β Nb-phase provides for its state of equilibrium, and particle size distribution below 0.1 μm. Such a structure of the alloy imparts thereto high corrosion resistance in high-temperature water, and ductility. Taking into account the fact that corrosion resistance is the principal performance characteristics of zirconium products made use of in the active core of nuclear reactors, the alloy structure comprising the β Nb-phase of an equilibrium composition imparts high corrosion-resistance characteristics to finished products in high-temperature water.

The iron/niobium ratio below 0.2 enables one to additionally isolate particles of iron-containing intermetallics Zr-Fe-Nb sized less than 0.3 μm and uniformly distributed in the α-solid solution, thus adding to the in-service hardness characteristics of finished products. In addition, the presence of intermetallics Zr-Fe-Nb in the alloy structure increases resistance of said alloy to nodular corrosion under boiling conditions, which is accompanied by thinning of the wall and hydrogenation of the cladding, as well as formation of thick oxide films which reduce heat conductivity thereof. Presence of intermetallics Zr-

Fe-Nb in the alloy structure reduces susceptibility of the alloy to nodular corrosion by 1.5 – 2 times.

With the iron/niobium ratio exceeding 0.2 the specified composition of the β Nb-phase is not observed, that is, the niobium proportion in the β Nb-phase is diminished, with the result that stability of anticorrosion properties is adversely affected.

An increased oxygen content of the alloy enhances creep- and radiation growth resistance at working temperatures by 2.5-6 times. Higher creep resistance is maintained in a neutron field as well. In addition, presence of oxygen stabilizes corrosion resistance and renders it less dependent on hot-working and heat-treatment conditions. As a result, anticorrosion and strength characteristics of the alloy are enhanced and stabilized due to oxygen-hardening of the α-solid solution.

Best Method of Carrying Out the Invention

To promote understanding of the present invention, given below are some specific exemplary embodiments thereof.

Example 1

Ingots were prepared from the alloy of the present invention, using the vacuum-arc melting technique. Then said ingots were subjected to a full processing cycle, namely, hot deformation (forging, rolling), β-quenching, press-forming in the upper portion of the α-region, and further to cold working involving intermediate α-annealing procedures to obtain a structure with a necessary set of phases adding to corrosion resistance and hardness, the principal part of which falls on the β Nb-phase with the particle size not in excess of 0.1 μm and the niobium content of from 75 to 95%.

In what follows the present invention is illustrated by Examples adduced in Tables 1, 2, and 3 of which Table 1 presents compositions of alloys according to the invention and to the prototype, Table 2 gives

characteristics of the β Nb-phase, and Table 3 indicates properties of said alloys. The alloy disclosed in the prototype is prepared using the process technique as claimed in the present invention.

Table 1

No of specimen	Alloying constituent, wt.%						Structure
	niobium	iron	oxygen	carbon	silicon	nickel	
1	1,1	0,01	0,1	0,008	0,006	0,005	α-solid solution, β Nb-phase
2	2,5	0,01	0,1	0,009	0,008	0,003	α-solid solution, β Nb-phase
3	2,5	0,5	0,05	0,02	0,02	0,006	α-solid solution, β Nb-phase, intermetallics Zr-Fe-Nb
4	2,0	0,1	0,03	0,001	0,002	0,02	α-solid solution, β Nb-phase, intermetallics Zr-Fe-Nb
5	1,5	0,01	0,2	0,015	0,005	0,02	O_2-hardened α-solid solution, β Nb-phase
6	0,5	0,005	0,15	0,04	0,1	0,02	O_2-hardened α-solid solution, β Nb-phase
7	0,4	0,004	0,02	0,01	0,01	0,008	α-solid solution
8 prototype	0,8	0,005	0,1	0,001	0,005	-	α-solid solution, secondary phase

Table 2

No of specimen	Characteristics of β Nb-phase particles in material of finished product		
	Particle size, μm	Particle spacing, μm	Nb content of β Nb-phase particles, %
1	0,04	0,15-0,20	85
2	0,05	0,12-0,15	90
3	0,08	0,12-0,17	85
4	0,06	0,12-0,15	85
5	0,06	0,12-0,17	80
6	0,03	0,18-0,20	75
7	-	-	-
8	-	-	-

Table 3

No of specimen	Creep rate, σ = 100 MPa at 350°C, %/h	Gain in weight in autoclave water at 350°C and 168 Pa for 3000 h, mg/dm^2	Radiation growth deformation at a fluence of $5.4 \cdot 10^{26}$ m^{-2} (E > 0.1 MeV), %
1	$3,3 \cdot 10^{-4}$	35-40	1,50-1,70
2	$2,0 \cdot 10^{-4}$	40-45	1,10-1,30
3	$6,0 \cdot 10^{-5}$	35-40	0,40-0,45
4	$9,0 \cdot 10^{-5}$	35-40	0,70-0,80
5	$7,0 \cdot 10^{-5}$	37-42	0,85-0,95
6	$1,8 \cdot 10^{-4}$	45-50	1,50-1,70
7	$7,0 \cdot 10^{-4}$	65-75	2,00-2,20
8	$4,5 \cdot 10^{-4}$	50-65	1,75-1,90

As is evident from the Examples presented before, with niobium content below 0.5 wt.% (Example 7), the β Nb-phase is not isolated whatever, which tells negatively on corrosion resistance of the alloy. Thus, e.g., the gain in weight of the test specimen in autoclave water

was equal to 65-75 mg/dm^2 rather than 35-50 mg/dm^2 for alloys comprising β Nb-phase. In addition, anticorrosion properties of the alloy are affected by the size of the β Nb-phase particles, particle spacing, volume proportion of particles and, last but not least, their niobium content. The most favorable, from the viewpoint of combining various properties, are alloy compositions as per Examples 1, 2, 3, 4, 5, and 6. In the alloys of Examples 1 and 2 their structure comprises α-solid solution with isolated β Nb-phase particles sized not in excess of 0.05 μm and the niobium content of 85-90% which corresponds to an equilibrium β Nb-phase composition. Corrosion resistance of said alloys exceeds that of an alloy with beyond-limiting values of the Nb and Fe content (Example 7) and of the prototype alloy (Example 8).

The alloys of Examples 3 and 4 further comprise intermetallics Zr-Fe-Nb (Example 3 with the Fe/Nb ratio of 0.2; Example 4 with the Fe/Nb ratio of 0.05), which add to the hardness of the alloy matrix, thereby increasing not only anticorrosion properties thereof, especially resistance to nodular corrosion, but also creep resistance and resistance to radiation growth deformation (Table 3).

The alloy of Example 5 further comprises a higher amount (0.2 wt.%) of oxygen, thus increasing creep- and radiation growth resistance and stabilizing corrosion resistance of the alloy due to hardening the α-matrix thereof (Table 3).

The alloy of Example 6 comprises a higher amount of oxygen and has a minimum niobium content which results in a reduced proportion of the β Nb-phase in the structure; however, insofar as the β Nb-phase particles are highly dispersed (having the size of 0.03 μm) and an equilibrium composition (a 75% niobium content), while the α-solid solution is oxygen-hardened, the characteristics of said alloy fall within permissible limits as to operational requirements. The structure of the material which may be obtained from the prototype alloy is not

specified. It is most probable that the composition of the secondary phase in a given structure is unequilibrium, whereby the properties of the material from the prototype alloy are inferior to those of the herein-proposed material.

Oxygen-hardening of the a-solid solution adds to the hardness and creep resistance of the alloy and stabilizes corrosion resistance thereof.

Hence use of the herein-proposed alloy allows of obtaining products having a homogeneous structure and finely divided particles of the β Nb-phase of an equilibrium composition uniformly distributed in said structure. As a result of forming such a structure, the material of the product features high corrosion-, radiation growth-, and creep resistance. Presence of intermetallics Zr-Fe-Nb in the alloy structure and of iron and niobium in the α-solid solution adds to creep- and radiation growth resistance of the alloy.

Industrial Applicability

The present invention can find most utility when applied for making products used in the active core of nuclear reactors. Moreover, said alloy may be used in the chemical and medicinal industries, as well as in other fields of engineering, wherein high corrosion resistance, ductility, breaking strength, and radiation resistance are required.

CLAIMS

1. A zirconium-based alloy for the components of the active core of nuclear reactors, comprising niobium, iron, oxygen, carbon, and silicon, featured by a structure comprising an α-solid zirconium solution, CHARACTERIZED in that said alloy further comprises nickel, with the following ratio of the constituents (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

and the structure of the alloy further comprises particles of the β Nb-phase which are sized below 0.1 μm and are uniformly distributed in said α-solid zirconium solution.

2. A zirconium-based alloy for the components of the active core of nuclear reactors, CHARACTERIZED in that its structure further comprises particles of intermetallics Zr-Fe-Nb.

3. A zirconium-based alloy for the components of the active core of nuclear reactors, CHARACTERIZED in that it comprises said constituents taken with the following ratio therebetween (on a weight percent basis):

niobium	0.5 - 3.0
iron	0.005 - 0.02
oxygen	0.03 - 0.12
carbon	0.001 - 0.02

silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the niobium content of the β Nb-phase particles being within 79 to 95%.

4. A zirconium-based alloy for the components of the active core of nuclear reactors, CHARACTERIZED in that it comprises said constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.02 - 0.5
oxygen	0.03 - 0.12
carbon	0.001 - 0.02
silicon	0.002 - 0.02
nickel	0.003 - 0.02
zirconium	being the balance,

the iron/niobium ratio being 0.05:0.2.

5. A zirconium-based alloy for the components of the active core of nuclear reactors, CHARACTERIZED in that it comprises said constituents taken with the following ratio therebetween (on a weight ratio basis):

niobium	0.5 - 3.0
iron	0.005 - 0.5
oxygen	0.1 - 0.2
carbon	0.001 - 0.02
silicon	0.002 - 0.1
nickel	0.003 - 0.02
zirconium	being the balance,

with the niobium content of the β-particles in the Nb-phase ranging between 75 and 95%, the α-solid solution being further oxygen-hardened.

6. A zirconium-based alloy for the components of the active core of nuclear reactors as claimed in any one of claims 2, 4, and 4, CHARACTERIZED in that the size of the particles of intermetallics Zr-Fe-Nb is below 0.3 μm.

ZIRCONIUM-BASED ALLOY FOR THE COMPONENTS OF THE ACTIVE CORE OF NUCLEAR REACTORS

Abstract

A zirconium-based alloy for the components of the active core of nuclear reactors comprises (on a weight percent basis): niobium, 0.5 – 3.0; iron, 0.005 – 0.5; oxygen, 0.03 – 0.2; carbon, 0.001 – 0.04; silicon, 0.002 – 0.1; nickel, 0.003 – 0.02; zirconium being the balance; the alloy structure is characterized by an α-solid solution and the β Nb-phase particles sized below 0.1 μm and having the niobium content of from 60 to 95%. The alloy may further comprise particles of intermetallics Zr-Fe-Nb with the Fe/Nb ratio of 0.05 – 0.2. The alloy structure may also be characterized by an oxygen-hardened α-solid solution and by the β Nb-phase particles, and may further comprise particles of intermetallics Zr-Fe-Nb sized below 0.3 μm.

COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

Attorney Docket Number: 25065-27

DECLARATION: As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled Zirconium - Based Alloy Elements Used in Nuclear Reactor Cores the specification of which:

[ ] is attached hereto.

[X] was filed on 08 October 1999 as PCT Application Number PCT/RU99/00368 and amended on _____ (if applicable.)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States listed below, and have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application on which priority is claimed:

(Number)	(Country)	Filed (Day/Month/Year)	Priority Claimed
99107802	RU	(22.04.99)	[X] Yes [ ] No
_____	_____	_____	[ ] Yes [ ] No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

(Application Serial No.)	(Filing Date)	(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT application(s) in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status - patented, pending, abandoned)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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